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(54) **A process for regenerating hydrocarbon oil hydrogenation catalysts.**

(57) A process for regenerating a hydrocarbon oil hydrogenation catalyst comprising a support of an inorganic substance and an active metal component by carrying out oxidative burning of the coke deposited on the catalyst so that the regenerated catalyst has a residual coke content of 0.5 to 10.0 % by weight is disclosed, and the process makes the catalytic activities of the catalyst recovered sufficiently, extends the lifetime of the catalyst in repeated use, prevents the catalyst from damage due to the regeneration, and, in hydrosulfurization processes, permits omission of presulfurization of the regenerated catalyst.

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However, since such oxidative burning for reducing the residual coke content to less than 0.5 % by weight requires to expose the catalysts to severe oxidation conditions, such as an atmosphere of a high oxygen concentration, elevated temperatures or a lengthy exposure to the oxidation conditions, problems including the damage to the catalysts are apt to arise even if the recovery of activity could be made by the removal of coke in its own way. In fact, the conventional methods involve the following problems.

Since the oxidative burning in the conventional regenerating methods is aimed at the complete removal of coke, even the active metal components on catalysts are oxidized excessively. In the case of the catalysts used for hydrodesulfurization reactions, sulfurized supported metal components and the metals attached during the reactions (vanadium, nickel and the like) are converted to oxides thereof. The oxidized metal components have considerably decreased melting and boiling points and become apt to melt or scatter at the elevated temperatures during the regeneration. This results in the change of pore structure, such as pore blockage, the decrease of the specific surface area and the decrease of the active sites due to the decrease or deactivation of the supported active metal components, thereby deteriorating the functions of the catalysts, including activity, every regeneration. That is, the conventional methods of regenerating this kind of hydrogenation catalysts involve the problem that the damage to the catalysts in every regeneration makes it difficult to maintain the catalytic functions, resulting in a considerably shortened lifetime of the catalysts in repeated use. Further, the excessive oxidation of the metal components to oxides by the oxidative burning necessitates at every regeneration a presulfurization of the catalysts as a pretreatment prior to use in hydrodesulfurization, or, depending on circumstances, necessitates a reactivation of the catalysts, such as a reduction treatment with hydrogen. Repeating such pretreatments of the catalysts every regeneration takes extra time and cost. Further, fluent repetition of the presulfurization makes it impossible to disregard the sulfur compounds discharged from regenerators, such as sulfur dioxide, and requires the installation of flue gas desulfurization systems.

In Japanese Patent Application Kokai Koho (Laid - open) Nos. 60 - 94145 and 50 - 123591 proposed are the methods of inhibiting the excessive evolution of heat during regeneration by carrying out the oxidative burning of coke by steps at a low oxygen concentration. Nevertheless, the methods cannot solve the above - described problems sufficiently since the residual coke is reduced to less than 0.5 % by weight by the regeneration so that the catalysts are oxidized excessively either.

Therefore, there has been an intense demand for a method of regenerating hydrocarbon oil hydrogenation catalysts which does not only remove coke by oxidative burning but also inhibits the damage to the catalysts so effectively as to maintain the catalytic functions including catalytic activity as much as possible and to enable the catalysts to stand repeated use as long as possible.

The present invention was made under these circumstances.

SUMMARY OF THE INVENTION

The object of the present invention is to solve these problems and to provide an improved method of regenerating hydrocarbon oil hydrogenation catalysts comprising inorganic supports and active metal components of Group VIA and/or VIII metals of the Periodic Table supported on the supports. More particularly, the object of the present invention is to provide an improved and advantageous method of regenerating the catalysts, by which the coke deposited on the catalysts is burnt off to a degree effective in a sufficient recovery of the catalytic functions including catalytic activity, and, at the same time, the damage to the catalysts due to the regeneration, namely the reduction of the original catalytic functions including activities, is inhibited, thereby extending the lifetime of the catalysts in repeated use and, in hydrodesulfurization processes, making the presulfurization of the regenerated catalysts unnecessary.

The inventors studied to attain the object in regenerating various kinds of supported catalysts which contain metal components having catalytic functions for the hydrogenation of hydrocarbon oils. Consequently, they found that without removing the coke deposited on the catalysts to such a low content less than 0.5 % by weight as in the conventional methods, the catalytic functions including catalytic activity could recover sufficiently by removing the coke to some degree. They further found that since the removal of coke became difficult rapidly as the residual coke content approached 0 %, such a reduction of the residual coke content to less than 0.5 % by weight as in the conventional methods required an oxidative burning of coke under drastic conditions, so that the above - described various problems arose due to the excessive oxidation of the catalysts. Thus they hit on the idea that if the target residual coke content was not the very little content of less than 0.5 % by weight but rather at a content enough for the recovery of the activity, the oxidative burning of coke could be carried out under more moderate conditions without oxidising excessively the active metal components, and the damage to the catalysts due to the oxidative burning could be inhibited sufficiently. That is, they found that the object of the present invention could be

nickel - cobalt - molybdenum - tungsten - alumina catalysts. These catalysts are suitable catalysts not only for hydrodesulfurization but also for other hydrogenation reactions, such as hydrocracking, hydrodenitrification and hydro-refining.

The catalysts which may be regenerated by the process of the present invention are not limited to those above exemplified, and the process of the present invention may be applied to the regeneration of other various hydrogenation catalysts, such as platinum - alumina catalysts, platinum - zeolite catalysts, platinum - silica catalysts or palladium - silica catalysts, which are effective in hydrocracking or hydrogenation reactions.

In addition to the above-described Group VIA and VIII metals and inorganic substances as the support components, the hydrogenation catalysts including the catalysts above exemplified may further contain other components.

The method of the preparation of the hydrogenation catalysts is not particularly limited, and the catalysts to be regenerated by the present invention may be prepared by various methods including known methods. For example, the active metal components may be supported by using any method, for examples by known methods, such as impregnation, ion-exchange or kneading.

The uses of the hydrogenation catalysts to be regenerated by the process of the present invention is not particularly limited, and in general, the regeneration process of the present invention is particularly suitable for the hydrogenation catalysts used in the processes of hydrocracking, hydrodesulfurization, hydrodenitrification or hydro-refining various hydrocarbon oils, such as naphtha, gasolines, kerosenes, gas oils, vacuum gas oils, atmospheric residues, vacuum residues, oils derived from oil sands or oil shale, crude oils, catalytic cracking oils or coal liquefied oils. The reaction conditions of the hydrogenation reactions depend on other conditions including the kind of the material oil and the objective reaction, and cannot be specified uniformly. Typical reaction conditions are as follows: a reaction temperature ranging from 300 to 480 °C; and a partial pressure of supplied hydrogen ranging from 10 to 250 kg/cm². The reaction system is not particularly limited, and various systems, such as a fixed bed, fluidized bed, moving bed, suspension bed or boiling bed, may be employed.

That is, the regeneration process of the present invention is particularly suitable for regenerating the catalysts used for the processes above described. In general, the regenerated catalysts are used in the same reaction as that before the regeneration. However, it is also possible to use the regenerated catalyst for a different reaction from the reaction wherein the catalyst was used before the regeneration.

In the process of regeneration of the present invention, the coke deposited on the catalyst is removed by oxidative burning, and it is important to control the oxidative burning so that the residual coke content ranges from 0.5 to 10.0 % by weight, preferably from 1.0 to 5.0 % by weight. With the proviso that the residual coke content is expressed by the reduction in weight after calcining of the regenerated catalyst in an atmosphere of air at 550 °C for eight hours as a percentage of the calcined catalyst.

If the oxidative burning is performed excessively to reduce the residual coke content to less than 0.5 % by weight, the catalyst is exposed to excessively drastic oxidation conditions, for example, in an atmosphere of a high oxygen concentration, at high temperatures or in a long-term of oxidation atmosphere, and, even if the activity is recovered to some degree by the removal of the coke, other problems, such as damage to the catalyst, are apt to arise. When the oxidative burning is carried out to reduce the residual coke content to less than 0.5 % by weight, even the active metal components on the catalyst are also oxidized excessively. For example, in the case of the catalysts used for hydrodesulfurization, sulfurized metal components or metals attached to the catalysts during the reaction, such as vanadium or nickel, convert into oxides. The oxidized metal components have considerably decreased melting points and volatilization points and melt or scatter easily at the elevated temperatures during regeneration. This changes the pore structure (such as pore blockage), decreases the specific area and reduces the number of active sites (a decrease or deactivation of the active metal components), and the original catalytic functions, such as activity, are deteriorated every regeneration. Thus, there arises a problem of the shortened lifetime of the catalysts in repeated use. Further such an excessive oxidation by the oxidative burning as to convert the metal components into oxides necessitates, every regeneration, a presulfurization of the catalysts prior to their use in hydrodesulfurization or, according to circumstances, necessitates a reactivation of the catalysts, such as a reduction treatment with hydrogen. Repeating such pretreatments of the catalysts every regeneration takes extra time and cost. Further, fluent repetition of the presulfurization makes it impossible to disregard the generation of sulfur compounds, such as sulfur dioxide, discharged from regenerators, and requires the installation of flue gas desulfurization systems.

To the contrary, in accordance with the process of the present invention wherein the oxidative burning is controlled to make the residual coke content of the regenerated catalyst range from 0.5 to 10.0 % by weight, preferably from 1.0 to 5.0 % by weight, the catalytic functions including catalytic activity can be

(a) The method of hydrogenating a hydrocarbon oil (hydro-refining accompanied by hydrodesulfurization, hydrodenitrification and demetalization)

Hydrocarbon oil (material oil):

Arabian heavy vacuum residue having the properties as shown in Table 2 (content of vacuum residues having boiling points of 525 °C or higher: 100 % by weight)

Reaction conditions:

Reaction temperature: 450 °C ,
Partial pressure of hydrogen (initial pressure): 85 kg/cm²G
Ratio of catalyst/material oil: 10 g/80 g
Reaction time: one hour

Reactor: 300 cc autoclave

Each of the hydrogenations before and after regeneration was carried out by introducing 80 g of the material oil and 10 g of one of the catalysts above described into a 300 cc autoclave, followed by allowing to react them for one hour at 450 °C and at an initial hydrogen pressure of 85 kg/cm²G.

(b) Regeneration conditions (conditions of oxidative burning)

Regeneration conditions

Regeneration temperature: 640 °C
Regeneration gas: air
Introducing velocity of regeneration gas: 1000 Ncc/hr/gram (catalyst)
Regeneration apparatus and system: fluidized-bed
regeneration system by using a 1000 cc fluidized-bed regenerator
Regeneration time: as listed in Tables 3 to 5

The regenerations of the catalysts were carried out by filling a 1000 cc fluidized-bed regenerator with the catalysts used for the hydrogenation (a) and conducting oxidative burning in a fluidized-bed system at 640 °C, while air was being passed through the regenerator at a supply velocity of 1000 Ncc/hr per gram of the catalysts.

The results obtained from Examples 1-6 and the Comparative Examples 1-5 are listed in Tables 3-5.

TABLE 1

	Supported metals	Supports
Examples 1, 2, 5, 6	Ni(3 wt%) - Mo(8 wt%)	Alumina (100 wt%)
Comparative examples 1, 2	Ni(3 wt%) - Mo(8 wt%)	Alumina (100 wt%)
Examples 3, 4	Co(3 wt%) - Mo(8 wt%)	Alumina - silica(50 - 50 wt%)
Comparative examples 3, 4, 5	Co(3 wt%) - Mo(8 wt%)	Alumina - silica(50 - 50 wt%)

TABLE 3

	Examples		Comparative Exs.	
	1	2	1	2
Catalyst components				
Supported metals (wt%)	Ni-Mo (3-8)	Ni-Mo (3-8)	Ni-Mo (3-8)	Ni-Mo (3-8)
Support (wt%)	Alumina (100)	Alumina (100)	Alumina (100)	Alumina (100)
Repeated numbers of reaction and regeneration	1	20	1	20
Regeneration time (hour) (oxidative burning time)	8.0	8.0	10.0	10.0
Residual coke content on a regenerated catalyst (wt%)	2.0	2.0	0.0	0.0
Ratio of the volume of pores of 0-500 Å in a regenerated catalyst based on that in a fresh catalyst (%)	88.4	83.2	86.4	35.5
Specific area of a regenerated catalyst (m ² /g)	126	115	89	35
Mo content of a regenerated catalyst (wt%)	8.0	7.8	7.0	3.8
SO ₂ concentration in the gas emerged from the regenerator (ppm)	123	120	520	530
Reaction products from hydrogenation				
Gas (C ₁ -C ₄) wt%	11.5	11.7	12.2	12.6
Naphtha (C ₅ -171 °C) wt%	17.0	17.2	17.9	18.0
Kerosene and gas oil (171-343 °C) wt%	31.2	30.8	29.6	26.6
Vacuum gas oil (343-525 °C) wt%	20.8	20.6	19.5	19.6
Vacuum residue (525 °C -) wt%	9.0	9.0	9.0	9.1
Solids insoluble in heptane wt%	10.5	10.7	11.8	14.1

TABLE 5

	Examples		Comparative Ex.
	5	6	5
Catalyst components			
Supported metals (wt%)	Ni-Mo (3-8)	Ni-Mo (3-8)	Ni-Mo (3-8)
Support (wt%)	Alumina (100)	Alumina (100)	Alumina (100)
Repeated numbers of reaction and regeneration	20	20	1
Regeneration time (hour) (oxidative burning time)	8.4	7.1	6.8
Residual coke content on a regenerated catalyst (wt%)	0.6	9.5	12.5
Ratio of the volume of pores of 0-500 Å in a regenerated catalyst based on that in a fresh catalyst (%)	76.2	35.0	25.0
Specific area of a regenerated catalyst (m ² /g)	93	76	29
Mo content of a regenerated catalyst (wt%)	7.4	8.0	8.0
SO ₂ concentration in the gas emerged from the regenerator (ppm)	180	130	115
Reaction products from hydrogenation			
Gas (C ₁ -C ₄) wt%	11.9	12.4	12.2
Naphtha (C ₅ -171 °C) wt%	17.4	17.6	17.9
Kerosene and gas oil (171-343 °C) wt%	30.4	29.6	27.6
Vacuum gas oil (343-525 °C) wt%	20.4	19.7	19.5
Vacuum residue (525 °C -) wt%	8.9	8.9	9.0
Solids insoluble in heptane wt%	11.0	11.8	13.8

Claims

1. A process for regenerating a hydrocarbon oil hydrogenation catalyst which comprises a support having an inorganic substance and an active metal component selected from the group consisting of a Group VIA metal of the Periodic Table, a Group VIII metal of the Periodic Table and a mixture thereof, supported on the support, which comprises carrying out oxidative burning of coke deposited on the catalyst, the oxidative burning of the coke being controlled so that the regenerated catalyst has a



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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 7833

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 310 163 (SHELL) * abstract * * page 3, line 4 - line 29 * * page 3, line 45 - line 56 * * example 1 * ---	1-11	B01J38/12 B01J23/94
X	US-A-4 751 210 (DE AGUDELO ET AL) * abstract * * column 5; table III * * column 3, line 44 - line 53 * ---	1-11	
D,A	FR-A-2 255 956 (HICKMAN ET AL) -----	1-11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 13 JANUARY 1993	Examiner LO CONTE C.	
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